I- INTRODUCTION

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A- Electrochemical Studies on Some Quinazoline Phenyl Hydrazone Derivatives.

1.1 Definition

Corrosion in a broad sense signifies the whole range of reactions between metals and their environments. Uhlig (1) describes corrosion as the reaction of a solid with environment. It is now generally accepted that corrosion is a reversion or a partial reversion from the metastable condition of the metal to stable condition of the mineral accompained by the reduction in the free energy of the system. It is the commonest electrochemical phenomenon experienced in day – to – day living. Common examples are rusting of iron and steel, tarnishing of silver and copper etc.

1.2 Classification of Corrosion

Corrosion of metals can be broadly calssified as (i) dry or chemical corrosion and (ii) wet or electrochemical corrosion

1.2.a. Dry or Chemical Corrosion

A dry corrosion results because of the reaction of metals with dry air or oxygen resulting in chemical corrosion. High temperature oxidation of metals and tarnishing of metals like copper and silver are due to this type of corrosion. Lately, this type of corrosion is also considered as an electrochemical process.

1.2.b. Wet or Electrochemical Corrosion

Wet or electrochemical corrosion occurs only in the presence of electrolytic solution. The reaction takes place at the metal-solution interface due to the presence of heterogenity of the metal surface, which creates local anodic and cathodic sites in the metal surface.

The nature and the extent of corrosion depend on the metal and environment. The most important factors which influence corrosion are: (1) Nature of the metal, (2) Nature of the environment, (3) Electrode potential, (4) Nature of the corrosion products formed, (5) Hydrogen overvoltage, (6) Concentration of various ions in the solution, (7) pH, (8) Amount of dissolved oxygen, (9) Conditions of flow of the solution and (10) Temperature.

1.3 Theories of Corrosion

The corrosion of metals in aqueous solutions is an electrochemical process. The first paper to explain the mechanism of corrosion was described by Wollaston (2) as early as in 1801. Whitney (3) in 1903, gave the most acceptable electrochemical theory of corrosion. The acid theory was proposed by Calvert and Walkar (4), Cederholm *et al,* (5) independently. The colloidal theory was proposed by Friend (6). The chemical attack theory was proposed by Bengough and Stuart (7). Subsequently Reddie and Linderman,(8) proposed the biological theory. All the above theories have been proved to be a part of the electrochemical theory. So only the electrochemical theory is generally accepted by everybody and applied to different corrosion processes.

Wollaston(2) proposed an electrochemical theory of corrosion which was initially developed by De La Rive(9) and then confirmed by Ericson Aure'n and Palmer(10) and rediscovered by Whitney(3) in 1903.

Tenard (11) confirmed that iron does not decompose water when both of them are perfectly pure. But once oxidation started, it can continue by the action of water alone.

De La Rive (12) noticed the striking difference in the behaviour of the action of sulphuric acid on pure zinc and impure metal. He concluded that impure zinc was vigorously attacked due to galvanic couple formed between zinc and its impurities. Later he extended his theory for the atmospheric corrosion of metals and concluded that corrosion was electrochemical in nature. In 1827, Becquerel (13) said that a cell could be produced by putting a metal in one electrolyte of two different concentrations and Mellet (14) utilised this in 1840 to explain the localized corrosion of iron casting in a tidal wave system. Adie (15) reported that cells were formed due to difference in oxygen concentration. Evans (16) succeeded in demonstrating these differential aeration cells.

Whitney(3) worked on the problem of corrosion of steel pipes in water and concluded that the process was electrochemical in nature since iron passed into the solution as ferrous ions, and corrosion rate was shown to be governed by the electromotive force of the cell set upon the iron surface. Evans and Hoar (17) gave evidence for the electrochemical setup on steel vertically immersed in steel plate in potassium chloride solution by measuring the current passing between the lower and upper portions of the steel plate. They also gave the potential vs. current curves for both the anodic and cathodic regions set upon the steel which is now known commonly as Evans diagram (Fig. 1.1).

The current corresponding to the intersection point known as corrosion current ($I_{corr.}$), correlated well with the rate of dissolution of metal obtained by the weight loss method.

Ericson-Aure'n and Palmer(10) developed an equation for the rate of dissolution of zinc in acid based on De La Rive's theory of local galvanic elements and Nernst's formula for electromotive force. Based on the findings of De La Rive, Evans(16) believed that corrosion was caused by local galvanic elements as a result of its structural inhomogenity or their chemical nature. They said that the surface of the metal undergoing corrosion exhibited a complex multi electrode system.

Trends in corrosion research changed rapidly over the years. In the fifties, polarization studies and their applications had been the topic of interest (18-20) . In the seventies corrosion research was concentrated on the mechanistic studies on metal dissolution, localized corrosion and high temperature corrosion (21-27). In recent years corrosion research has been divided into several recent fields. The optical techniques have revolutionized the fields. Surface analytical techniques give more insight into the understanding of the nature and influence of surface oxides on the corrosion of metals and alloys. These techniques are helpful to characterize thickness, structure and composition of films. Computers(28,29) and micro processors (30) find application in analyzing corrosion data.

The ultimate objective of all these investigations is to minimize corrosion failures.

1.4 Thermodynamic Principle of Corrosion

In most of the cases, metallic state represents a state of high energy. Therefore metals have a natural tendency to react with other substances and go back to lower energy states with subsequent release of energy. Except noble metals, all other metals show decrease in free energy by undergoing reaction with the environment.

Thermodynamic stability of chemical compounds is determined by the sign and the change in free energy (ΔG) when they are formed from simple substances. If G_1, corresponds to the initial free energy of materials and, 'G_2' that of the reaction products then $G_2 - G_1 = \Delta G$.

If $G_1 > G_2$, ΔG is less than zero (negative value) then the corresponding compound is stable(31). The literature shows that only the oxides Au_2O_3, AgO and Ag_2O_3 are thermodynamically unstable under standard conditions. Thermodynamic approach has been widely used for understanding the fundamental corrosion problems, though it does not provide any information on the kinetics of corrosion processes.

1.5 Kinetics of Corrosion Processes

The study of kinetics of corrosion reaction is very important, since it is necessary to determine the corrosion rate.

Thermodynamic (discussed in the previous section) assumes the metal is in equilibrium with its own ions, and, thus, at its equilibrium potential. Corroding systems however, are not in equilibrium since an irreversible electrode potential deviates considerably from the equilibrium potential of the metal with its ions. The new potential is accompanied by electrode reaction consisting of charge transfer, mass transport and other related phenomena. The current accompanying such a reaction, the corrosion current i_{corr}, is a measure of the rate of corrosion process.

1.5.a Basic Concepts

When an electrode is at equilibrium the rate per unit area of the forward reaction is equal to that of backward reaction.

$$M \underset{\overleftarrow{i}}{\overset{\overrightarrow{i}}{\rightleftharpoons}} M^{n+} + ne$$

where $\overrightarrow{i}$ and $\overleftarrow{i}$ represent the forward and backword current density. When those current densities are equal, net transfer of charge does not occur.

$$i_o = \overrightarrow{i} = nF\overrightarrow{K} \; \exp. [\, (1-\alpha)\, nFE_{eq} / RT \,] =$$
$$\overleftarrow{i} = nF\overleftarrow{K} \; \exp. [\, -\alpha\, nFE_{eq} / RT \,]$$

where i_o is the equilibrium exchange current density, α is the transfer coefficient, and the electrode potential is said to be unpolarized,

i.e., $E = E_{eq.}$ and $\eta = E - E_{eq.} = 0$

where η is the activation overpotential.

In this situation no net metal loss occurs, though surface reactions are progressing. This case takes place when the height of the energy barrier is the same for the forward reaction and the backward reaction, see Figure (1.2). If the potential, E, is removed from the equilibrium, $E_{eq.}$, then,

$$\overrightarrow{i} \; \# \; \overleftarrow{i} \; \# \; i_o$$

This potential is called non – equilibrium potential and the net current density at the electrode equals [$\overrightarrow{i} - \overleftarrow{i}$]. In Figure (1.3) the potential energy vs. distance curves that for this situation the height of energy barrier of the backward reaction is higher than that of the forward reaction. Charge transfer reaction can be expressed through Butler – Volmer (32) equation.

$$i = \overrightarrow{i} - \overleftarrow{i} = nF\overrightarrow{K} \; [\, (1-\alpha)\, nF(E - E_{eq.})/ RT] - nF\overleftarrow{K} \exp[-\alpha\, nF\, (E - E_{eq.})/RT\,] \qquad (1.1)$$

$$i = i_o = \{\exp\, [(1-\alpha)\, nF\, (E - E_{eq.})/RT]\, - \exp.[\alpha\, nF\, (E - E_{eq.} / RT]\} \qquad (1.2)$$

The corrosion rate can be obtained from corrosion current $i_{corr.}$ from equation (1.3):

$$i = i_{corr.}\, [\exp \eta_a / \beta_a - \exp \eta_c / \beta_c\,] \qquad (1.3)$$

where β_a and β_c are the symmetry factors.

If the rate of the electrode process is entirely charge-transfer controlled and η is sufficiently large so that $i_a >> i_c$ or $i_c >> i_a$, then the relationship between i and η follows Tafel equation (33)

$$\eta = b \log i / i_o \qquad (1.4)$$

where η in this case is the activation overpotential and b is Tafel slope.

1.5.b Mixed Potential Theory

When an electrode or metal sample is freely immersed in electrolyte, there are two or more oxidation-reduction systems with different equilibrium potentials and different exchange current densities.

For example, an iron electrode in acid solution produces the following half cell reactions.

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (1.5)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (1.6)$$

Since, the hydrogen evolution (cathodic reaction) takes place on the iron substrate, the result is a mixed potential between the equilibrium potential of Fe / Fe^{2+} electrode and the equilibrium potential of H^+ / H_2 electrode.

For corrosion reaction to proceed the rate of both reactions must be equal with no accumulation of charge during the electrochemical reaction. By plotting the current density on a logarithmic scale for example, for the two half reactions, (1.5) and (1.6) against the applied potential, polarization lines will be linear, in accordance with Tafel equation.(33)

This diagram is very important since it considers both, the thermodynamics (represented by the potential E) and the kinetics of corrosion reaction (represented by current density I).

Figure (1.4) is a modified version of Evans diagram*(16)* (Stern diagram)*(19)* notably by inclusion of exchange current density (i_o) which has led to a more accurate representation of corrosion. It is clear that the corrosion current density ($i_{corr.}$) can be obtained by extrapolating the Tafel regions back to E_{corr}.

Figure (1.5) is a schematic diagram showing how the corrosion rate is considerably increases when the exchange current density (i_o) for the cathodic reaction has increased, for instance, due to impurities of higher, i_o for H^+ / H_2 half reaction. It could be regarded as the cathodic polarization on pure metal, B and C are on different metal (impurities).

Figure (1.6) shows the effect of pH on $E_{eq.}$ and i_o for H^+ / H_2, an increase in pH (decrease a H^+) lowers $E_{eq.}$ and decreases, $i_{o\,c}$ subsequently $i_{corr.}$ and $E_{corr.}$ decrease. Where anode and cathode areas are considerably different, it is very important to consider the area effect on the rate of the anodic and the cathodic reaction on each individual area separately.

1.6 Mechanism of Electrochemical Reaction (33):

Significant contributions of Bockris, Frumkin, Parsons, Vetter, Gerischer, Conway, Bagotsky, Delahay and Wroblowa have made it possible to develop the diagnostic criteria for the elucidation of the mechanisms of electrochemical reactions. Stages involved in the mechanism determination are:

1) Elucidation of overall reaction by coulombic analysis.

2) The identification of the entities in solution.

3) Determination of rate determining step (rds).

The parameters required for identification of rds are (a) reaction orders, (b) transfer coefficients and (c) stoichiometric number.

The concept of reaction order has been developed by Vetter (34) and the same is determined from the plots of log anodic or cathodic current densities against log concentrations of any species taking part in the electrode reaction at constant electrode potential.

$$Z_{Ai} = [\,(d \log i)/(d \log C_{Ai})\,] \quad A_j \# I, i, \Delta\text{Ø} \qquad (1.7)$$

After determining the reaction orders of all components of the overall reaction, one writes down various seemingly possible consecutive reaction sequences in which the overall reaction might be brought about.

The determination of transfer coefficient, is helpful for determining the number of electrons transferred in the rds. It is obtained from the slope of the plots of η vs log current at a constant concentration of reactants. These coefficients are invariably multiples of 0.5 for determining the number of times (rds) to occur for one act of overall reaction, the stoichiometric number (υ) is got from the relationship:

$$\upsilon = n / (\alpha_a + \alpha_c)$$

Besides the above mechanistic parameters, determination of exchange current is essential for understanding the kinetics of the process. Various techniques have been developed for studying the kinetics of electrode process.

The theory and application of these methods are reviewed by Yeager *et al.* (35) and Damaskin (36).

In corrosion process, normally observed electrode reactions are hydrogen evolution, oxygen reduction and metal dissolution.

$O_2 + é \rightleftharpoons O_2^-$ $O_2^- + H^+ \rightleftharpoons HO_2$ $HO_2 + é \rightleftharpoons HO_2^-$ $HO_2^- + H^+ \rightleftharpoons H_2O_2$	$O_2 + 2H^+ + 2\,é \rightleftharpoons H_2O_2$ (1.15)
$H_2O_2 + é \rightleftharpoons OH + OH^-$ $OH + é \rightleftharpoons OH^-$ $2[OH^- + H^+ \rightleftharpoons H_2O]$	$H_2O_2 + 2H^+ + 2é \rightleftharpoons 2H_2O$ (1.16)

$$O_2 + 4H^+ + 4\,é \rightleftharpoons 2H_2O \qquad (1.17)$$

The second mechanism utilises the formation of surface oxide, hydroxides, oxyhdroxides of the metal.

$$2 \times (M + H_2O \rightleftharpoons M\text{-}O + 2H^+ + 2\,é) \qquad (1.18)$$

$$\underline{M\text{-}O + M\text{-}O \rightleftharpoons 2M + O_2} \qquad (1.19)$$

$$2H_2O \rightleftharpoons O_2 + 4H^+ + 4é \qquad (1.20)$$

1.7 Inhibition of Corrosion of Metals in Acidic Medium

Introduction

One of the most extensively studied topic in the field of corrosion is inhibition. Several books have been published on this subject (42-44). The University of Ferrara, Italy, conducts a symposium on corrosion inhibition in five years (45). The international seminars on corrosion discuss the developments and applications of corrosion inhibitors (46, 47). Trabanelli and Carassiti (48) and Sanyal (49) have reviewed this phenomenon along with Weber (50) and Suzuki (51). Various books on corrosion review the subject in a precise manner (52-54). These show that the information on this subject is extensively available and also the importance of this topic.

1.7.a. Definition

The NACE defines inhibitor as a substance which retards corrosion when added to an environment in small concentrations *(55)*.

1.7.b. Classification and Mode of Inhibition

Inhibitors are classified as acid, neutral, alkaline and vapour phase inhibitors depending upon the environment in which they are used. Based on the mechanisms they are classified as anodic, cathodic or mixed type inhibitors. As we are interested only in acid inhibitors other inhibitors are not discussed here.

1.7.c Acidic Inhibitors

Acidic inhibitors are those chemical substances which are used to prevent corrosion in aqueous acid solutions. They are further classified into inorganic inhibitors and organic inhibitors.

1.7.c$_1$ Inorganic Inhibitors

Inorganic compounds such as As_2O_3 and Sb_2O_3 have been reported as inhibitors in acid media. The action of these compounds has been attributed to the deposition of the metal on iron and steel and rise the hydrogen overvoltage and then reducing the corrosion *(42)*. In strong acid solutions, Br^- and I^- ions have been found to be effective inhibitors*(56)*. This is due to more stable chemisorption of these ions because of the easy deformability of their electron shells *(57)*. Recently it is shown that the addition of heavy metal ions such as Pb^{2+}, Tl^+, Mn^{2+} and Cd^{2+} are found to inhibit the corrosion of iron in acids. This effect is attributed to the underpotential deposition of metal ions leading to complete coverage of Me-adsorbate on the iron surface *(58)*.

1.7.c_2 Organic Inhibitors

A large number of organic compounds have been found to be effective in acid media. Studies on the relation between the organic structure of inhibitors and their effectiveness in acid system have been made by many workers and summarised by Eldredge *et al.*, (59) and Douty(60). It has been found that these inhibitors have O, N or S atoms in their structures which will donate electrons for bonding with metal surface. Mostly the inhibition by organic compounds is due to adsorption, electrostatic, chemisorptive interaction and also due to adsorption resulting from л orbital interaction with the metal (61, 62).

Electrostatic adsorption depends on the potential of zero charge (pzc) of metal surface and also on the position of corrosion potential with respect to pzc. The adsorption of organic inhibitor depends on the sign and magnitude of 'rational' corrosion potential (Ø) ($\O=E_{corr.}-E_{eq}$) and on the sign of the charge on the inhibitor molecule. Adsorption of cationic compounds requires a negative (Ø) potential, whereas a positive 'Ø' potential is required for adsortion of anionic compounds. It has been shown for nitrogen containing compounds, the inhibition efficiency for iron in acid is higher when the Ø potential is more negative (63).

Chemisorption of an organic molecule involves a bonding between the metal and adsorbed molecules through an atom containing an unshared electron. It depends on the nature of the metal, the molecular structure of the inhibitor molecule and the chemical nature of the bonding atom. In addition, such factors as the lattice parameter of the metal and inter-atomic distance between two or more bonding atoms in the inhibitor molecule are quite often important in chemisorption. Chemisorption is slow and temperature dependent.

Inhibitor molecules containing aromatic nucleus, double bonds, or triple interact with metal by the л – bond orbitals. This type of interaction is independent of potential, but it is temperature independent. Hackerman and Hurd (64) correlated the inhibition efficiency with the number of carbon atoms in the ring.

1.7.d Recent Approach on The Study of Inhibitors

The recent approach (65) is based on the mechanism of inhibitive action, has however divided the corrosion inhibitors into four major categories:

1) Barrier layer formers
2) Neutralizers
3) Scavengers
4) Miscellaneous

1) Barrier LayerFormers

These materials form barrier layers on the corroding metal surface and reduce the corrosion rate. This type forms the largest category of corrosion inhibitors. Barrier layer formers have been further classified into oxidizers, adsorbed layer – formers and conversion layer formers. In general these inhibitors are effective in reducing both the cathodic and anodic reaction rates except for the oxidizing inhibitors which shift the corrosion potential of the metal to more positive values at which a stable oxide (or) hydroxide is formed and protected the metal surface.

2) Neutralizers

These inhibitors remove the hydrogen ions from the corrosive environment there by reducing the corrosivity of the environment and hence the concentration of the cathodic reactant. These inhibitors are used in the treatment of boiler water, oil field applications etc.

3) Scavengers

These are similar to neutralizers but used to remove corrosive species other than hydrogen ions. Typical example is hydrazine in boiler systems which removes traces of oxygen which is a cathodic reactant.

4) Miscellaneous

These inhibitors include materials such as scale inhibitors and biological growth inhibitors which reduce corrosion by interfering with other processes.

1.7.e Synergism (66)

Examples of corrosion inhibition by simple anions have been noted for some time. In 1930, Walpert (67) showed that the addition of HCl slowed the corrosion rate of mild steel in sulphuric acid by 78%; however the presence of certain anionic species often enhances the efficiency of an organic inhibitor, resulting in greater inhibition than achieved by either additive alone. Malowan (68) patented the use of mixtures of iodide ion and organic amines for inhibition of the corrosion of steel in phosphoric acid.

Inhibition by anions and the synergistic effect of some anions and organic compounds is a complex phenomena, and it is doubtful if one mechanism accounts for all the observations. Passivating potentials imposed by redox couples (69) account for the mechanism of ions in some systems. Mixed oxide formation (70) also is a plausible mechanism for other systems. A third mechanism is the strong adsorption of anions in metal surfaces. This is the one which properly explains synergistic effects between anions and organic inhibitors and inhibition in the absence of alternate redox couples and/or bulk oxide formation.

The term "synergism" can be defined as the marked reinforcement of the inhibiting action of one inhibitor by the addition of small amounts of a second inhibitor, even though the second inhibitor is less effective when used alone.

1.7.f Adsorption Isotherms

An adsorption isotherm gives the relationship between the coverage of an interface with an adsorbed species (the amount adsorbed) and the concentration of the species in solution. Various adsorption isotherms have been formulated. Interpretation of adsorption and performance of organic inhibitors can be evidenced by fitting the data to one of the adsorption isotherms. From a suitable plot, the free energy of adsorption of the organic inhibitor is obtained.

1.7.g Nature of Inhibition of Corrosion

Electrochemical studies have shown that inhibitors in acid solution may affect the corrosion reactions of metal in following ways:

1.7.g_1 Formation of A Diffusion Barrier

The adsorbed inhibitor may form a surface film which acts as a physical barrier to restrict the diffusion of ions or molecules to or from the metal surface and to retard the corrosion reactions. This effect occurs particularly when the inhibitor species are large molecules like proteins such as gelatine, agar-agar etc. Similar effects also occure when the inhibitor can undergo reaction to form a multimolecular surface film as in the case of acetylinic compounds and sulphoxides.

1.7.g_2 Blocking of Reaction Sites

The interaction of adsorbed inhibitor with surface metal atoms may prevent these metals atoms from participating in either the anodic or cathodic reaction of corrosion. The simple blocking effect decreases the number of surface metal atoms at which these reactions can occur, and hence the rates of these reactions, in proportion to the extent of adsorption. The mechanism of the reactions is not effected and the Tafel slope of the polarization curve remain unchanged.

1.7.g_3 Participation in Electrode Reaction

Electrode reactions of corrosion involve the formation of adsorbed intermediate species with surface metal atoms, just as adsorbed hydrogen atoms in the hydrogen evolution reaction, adsorbed (FeOH) in the iron dissolution reaction etc. The presence of adsorbed inhibitors will interfere with the formation of these adsorbed intermediates and hence the electrode processes may then proceed by alternative paths through intermediates containing inhibitor. In these processes, the inhibitor species act in a catalytic manner and remain unchanged, since participation by the inhibitor is generally characterised by a change in Tafel slope observed for the process. Studies of the anodic dissolution of iron in the presence of some inhibitors such as benzotriazole, and o-phenonthroline have indicated that the adsorbed inhibitor (In) participates in the reaction, probably forming complexes of the type $(Fe\text{-}In)_{ads}$ or $(Fe\text{-}OH\text{-}In)_{ads}$.

The dissolution reaction proceeds less rapidly via the adsorbed inhibitor complexes than via $(Fe\text{-}OH)_{ads}$ and so anodic dissolution is inhibited and an increase in Tafel slope is observed for the reaction.

Similarly, inhibitors such as phenyl thiourea, and benzaldehyde derivatives have been found to affect the mechanism of hydrogen evolution reaction.

Besides the above influences, the adsorbed inhibitor may also influence the corrosion reaction in following ways (71, 72):

a) The adsorbed inhibitors may increase the separation between reaction zone and electrode surface.

b) The adsorbed inhibitors may change the potential distribution in the diffused part of double layer.

c) The adsorbed inhibitors may interact with the reaction species.

The rate expressions and testing methods of the above all models of inhibition have been derived and applied to the inhibition of electrochemical reactions especially in the discharge of metals ions.

Corrosion Inhibition of Metals in Presence of Quinazoline Phenyl Hydrazone Derivatives and Related Compounds

The influence of some organic acid hydrazides, namely salicylic acid hydrazide (SAH), anthranilic acid hydrazide (AAH), benzoic acid hydrazide (BAH) and cinnamic acid hydrazide (CAH) on the corrosion inhibition of mild steel in the presence of 1 N HC1 was studied (73). The adsorption of all the hydrazides on mild steel surface in the acid solution was found to obey Temkin's adsorption isotherm. The values of activation energy and free energy of adsorption of all the hydrazides were also calculated. The potentiodynamic polarization studies indicated that all the hydrazides except SAH are mixed inhibitors.

It has been observed from weight loss and hydrogen gas evolution measurements that 4-phenylsemicarbazide (4PSC) and semicarbazide (SC) actually have very significant effects on the corrosion of mild steel in hydrochloric acid (74). 4PSC and SC tend to inhibit the corrosion of mild steel in hydrochloric acid to a remarkable extent, with 4PSC exhibiting a higher maximum inhibition efficiency (82%) than that of SC (66%). Generally, the inhibition was found to increase with increasing the inhibitor concentration, with a decrease in temperature and decrease in the first-order rate constants obtained at 30°C and 40°C. The Physisorption mechanism of adsorption has been proposed for the inhibitors and the difference observed in the inhibition behaviour of the compounds has been explained. The inhibition behaviour of these compounds also obey the Freundlich adsorption isotherm equation.

The effects of benzoin (BN), benzil (BL), benzoin-(4-phenylthiosemicarbazone) (BN4PTSC) and benzil -(4-phenylthiosemicarbazone) (BL4PTSC) on the corrosion of mild steel in hydrochloric acid have been studied (75). Weight loss and hydrogen evolution measurements reveal that BN exhibits a higher maximum inhibition efficiency than BN4PTSC, BL and BL4PTSC. Generally, inhibition was found to increase with increasing the inhibitor concentration and temperature. Chemical adsorption mechanism has been proposed for the inhibitors and the difference in the inhibition behaviour of the compounds has been explained in terms of the solubility of the compounds as well as the strength of the inhibitor-metal bond.

The inhibition of the corrosion of aluminium in 2 N hydrochloric acid solution by some biacetylmonoxime hydrazone derivatives has been studied using weight-loss, thermometric and galvanostatic techniques (76). The three techniques gave concordant results. The inhibition efficiency of the additives increases in the order: I > II > III > IV > V. The inhibitors appear to function through general adsorption following the Langmuir adsorption isotherm. These compounds were excellent inhibitors for acidic corrosion of aluminium and inhibited both cathodic and anodic reactions.

The corrosion of aluminium in hydrochloric acid solution is retarded by the addition of some o-hydroxy acetophenone benzoyl hydrazone derivatives (77). This influence is studied by thermometric, hydrogen evolution and mass loss methods. The inhibition efficiencies obtained from the different methods utilized are in good agreement. The inhibitory charecter of the additives depends upon the concentration as well as the composition of the inhibitor. The degree of coverage (θ) of the adsorbed additives was determined from the reaction number values, and the results was found to obey the Langmuir adsorption isotherm.

The corrosion behaviour of iron in 1M HNO_3 containing furfural hydrazone derivatives was studied by electrochemical, polarographic and scanning electron microscopy measurements (78). Polarization data indicates that all inhibitors tested were of a mixed type, affecting both the cathodic and anodic processes. It was found that the compounds under consideration are adsorbed on the iron surface. The degree of surface coverage is influenced by the presence of functional groups and interaction between adsorbed molecules. Within the given homologous series the contribution of the functional group to adsorption increases with the length of the chain.

The inhibition characteristics of some thiazole derivatives against copper corrosion in acidic sulphate containing media have been investigated (79). The investigated thiazole derivatives were 5-benzylidene-2,4-dioxotetrahydro-1,3 -thiazole ($C_{10}O_2H_7SN$) and 5-(4' isopropylbenzylidene)-2, 4-dioxotetrahydro-l, 3-thiazole ($C_{13}O_2H_{13}SN$). In situ information on corrosion and inhibition processes at nanoscale range were obtained using scanning tunneling microscopy (STM) in combination with quartz crystal microbalance (QCM) measurements. XPS measurements were also performed to analyze the copper electrode surface. Based on these findings the role of molecular structure in corrosion inhibition has been discussed. The presence of the isopropyl group in the 5-IPBDT molecule produced far better protection against copper corrosion in acidic sulphate containing media than 5-BDT.

The effect of some benzene sulphonyl hydrazone derivatives on the corrosion of iron in 1M HC1 solution at 303K was investigated from polarization and weight loss techniques (80). A significant decrease in the corrosion rate of iron was observed by the presence of traces of these compounds. The corrosion rate (i_{corr}) was found to be a function of the nature and concentration of the inhibitor and temperature of the medium. The degree of surface coverage calculated from the results were used to evaluate the free energy of adsorption (ΔG°_{A}) of the inhibitors. All the inhibitors follow the Frumkin adsorption isotherm. The mechanism of inhibitor action has been discussed on the basis of adsorption and molecular polarization of the inhibitor. The observed experimental data indicate that all compounds tested were of mixed type, but the cathode is more preferentially polarized. The effect of temperature was studied in order to obtain the kinetic and thermodynamic parameters of the iron corrosion.

The effect of changing functional groups of some amides and thiosemicarbazone derivatives on their inhibition efficiency has been reported with a view to establishing a relationship between inhibitor efficiency and molecular structure, using the weight loss and hydrogen evolution techniques (81). The compounds used for this study are urea (U), thiourea (TU), acetamide (A), thioacetamide (TA), semicarbazide (SC), thiosemicarbazide (TSC), methoxybenzaldehyde thiosemicarbazone (MBTSC), 2-acetylpyridine-(4-phenyl) thiosemicarbazone (2AP4PTSC), 2-acetylpyridine-(4-methyl) thiosemicarbazone (2AP4MTSC), benzoin thiosemicarbazone (BZOTSC) and benzil thiosemicarbazone (BZITSC). All the compounds inhibited corrosion to varying degrees. It was found that the molecules which include a thiocarbonyl group, e.g. TU, TA and TSC, have higher inhibition efficiency than the corresponding compounds which do not, e.g. U, A and SC. The results (at 30°C and 40°C) indicate that the order of efficiency of the thiocompounds in solution and the extent of their tendency to adsorb on mild steel surfaces are as follows: TSC > TU > TA, whereas for the thiosemicarbazone derivatives, the order is BZOTSC > BZITSC > MBTSC > 2AP4MTSC < 2AP4PTSC. Physical adsorption mechanism has been proposed for all the inhibitors except MBTSC, BZITSC and BZOTSC, which are chemically adsorbed. The mechanism of corrosion inhibition considers the total molecular structure of the inhibitor, and the nature and spatial relationship of the different functional groups.

Quraishi *et. al.* (82) investigated a new corrosion inhibitor namely , 4 – salicylideneamino – 3 – hydrazino – 5 – mercapto – 1,2,4 – triazol (SAHMT), which has been synthesized and its influence on corrosion inhibition of oil well tubular steel (N – 80) and mild steel 15% hydrochloric acid (HCl) solution underboiling condition has been studied using weight loss method. Potentiodynamic polarization measurements clearly reveal that the investigated inhibitor is of mixed type and it inhibits the corrosion of both cathodic and anodic reactions and inhibits the steels by blocking the active site of the metal surface. The adsoroption of this inhibitor has been found to obey Temkin's adsorption isotherm.

Gokhale *et. al.* (83) studied the efficiency of 2- sulfhydryl methyl benzimidazole for inhibiting corrosion of Cu and α – brass in 1N HCl. The efficiency increased with increasing inhibitor concentration up to ≤ 500 ppm, exposure time 144 hrs., and decreasing temperature in the range 398-323 K. For brass at high temperatures the inhibitor accelerated the corrosion, especially at low concentrations. The inhibitor was effective because of the film formation. Dezincification of brass was responsible for the low inhibitor efficiency in HCl.

Soni *et. al.* (84) investigated the corrosion of Cu and Zn (Cu-36.7%Zn) in acid media. Dithioglycolic acid was found to be excellent corrosion inhibitor for the metals in HNO_3 and trichloroacetic acid. Diphenyl thiourea had inhibition efficiency of 60% for Cu in H_2SO_4. The inhibition efficiency was 60 – 70 and less for brass.

Sylvia *et al.* (85) investigated the corrosion of Cu electrode in deaerated 1M HCl in presence of Fe^{3+} ions, in the absence and presence of benzotriazole (BTAH) by weight loss measurements using a rotating disk electrode. The corrosion process was found to be controlled by the transport of Fe^{3+} ions to the electrode surface both in the absence and in the presence of BTAH. The inhibiting action is initiated at BTAH concentration of 10 mM and Langmuir adsorption isotherm is obeyed in BTAH concentration range 10-45 mM with an apparent equilibrium adsorption constant of $10M^{-1}$. Above this concentration, the Langmuir plot is not obeyed due to the formation of a multilayer. The surface films formed during the corrosion process were investigated by in situ and exsitu fluorescence and Raman spectroscopy and characterized as being composed of the polymeric [Cu(I)BTA] complex and $[Cu(I)Cl\ BTAH]_4$. The former as an inner layer response to the corrosion inhibition process.

Omer *et al.* (86) tested the inhibiting action of some Schiff bases on the corrosion of Cu and its alloys in HCl and H_2SO_4, solutions. The behaviour of electrolytic Cu, Al brass, and cupronickel also was tested. The corrosion media were 5% solutions of HCl and H_2SO_4. Weight loss determination and the recording of anodic and cathodic polarization curves were made. The schiff bases prepared from aliphatic amines stimulate Cu corrosion, where as those obtained from aromatic ones inhibit it. The inhibiting action is mainly exerted on the cathodic reduction reaction. The effect of the various schiff bases was explained on the basis of their stability and the effect of the different substituents in the aromatic ring.

Dinnappa *et. al.* (87) studied the corrosion of copper in $HClO_4$ solution containing various concentration (10^{-7} – 10^{-4} M) of benzoic p-toluic acid, p-nitro benzoic acid, phthalic acid and terephthalic acid at 30°C. The results showed that these compounds inhibit the corrosion even at trace concentration. The corrosion rate is a function of temperature, concentration and the nature of the inhibitor. The inhibitor efficiency calculated from the weight loss and polarization methods are in a good agreement. Thermodynamic parameters for the adsorption of inhibitors were evaluated by using the Bockris-Swinkels adsorption isotherm with n=5 as a configuration function. The corrosion inhibition is discussed regarding the adsorption of inhibitor on molecules at the metal / solution interface.

Fouda *et al.* (88) studied the effect of some substituted phenols as corrosion inhibiotrs for copper dissolution in 2N HNO_3 by weight loss and galvanoststic polarization techniques. Polarization data suggest that in the case of inhibitor, the cathode is preferentailly polarized under the influence of the external current. The inhibitor appears to function though general adsorption following the Langmuir adsorption isotherm. The inhibiting effect of tested compounds is due to the destruction of the HNO_2 formed and its interference with the cathodic reaction.

Subramanyam *et. al.* (89) explored the effect of quinine and strychnine on the corrosion of copper in H_2SO_4 using polarization and weight loss methods. The maximum corrosion inhibition (99%) was observed with 10^{-3}M strychnine. The weight loss and polarization techniques gave similar inhibition efficiency values. The adsorption followed the Bockirs – Swinkels adsorption. The increase in the anodic Tafel slope in the presence of inhibitors suggests the inhibition of both the anodic and cathodic reaction of the corrosion process. The negative free energy of adsorption and the high protection efficiency indicate a strong interaction between the inhibitors and the copper surface.

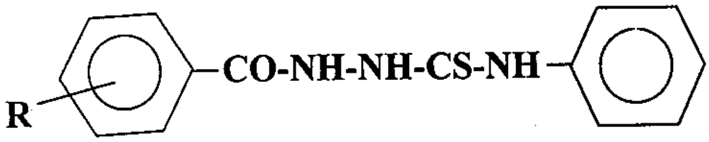
Trufanova *et. al.* (90) studied the effect of the salts of nitro derivatives of phenol and of oxyaromatic acids as corrosion inhibitors of copper . Corrosion tests showed that nitrophenolates of organic bases and the nitrocarboxylates of sodium and hexamethlenimine are effective inhibitors of copper corrosion in an aqueous solution (PH=7). The nitrocarboxylates of other amines are not effective inhibitors and some of them cause a stimulation of copper corrosion. Thus, the sodium and hexamethylenimine salts of nitro aromatic acids and organic salts of nitro-phenols are anodic inhibitors of copper corrosion. The protection is caused by physical adsorption and chemisorption on the metal and its oxide film, and also by the formation in the pores of an air – oxide film of insolube products of the reaction of copper ions and nitro-aromatic compounds.

Fouda *et. al.* (91) studied the effect of some triary1 and trialky1 phosphates as inhibitors of the corrosion of copper in nitric acid solution. The values of inhibitors efficiency from weight loss measurements are in good agreement with those obtained from polarization studies. Potential and polarization data indicate that the action of all compounds used are of mixed type, they hinder both anodic and cathodic reactions. The inhibitors appear to function through general adsorption following the Langmuir adsorption isotherm.

Talati *et. al.* (92) showed that the corrosion of copper in lactic acid increased in acid concentration. Buffalo milk and curd had no effect on copper corrosion. The addition of azo food dyes increased the lactic acid corrosion of copper. Saccharin accelerated corrosion in both dye free and coloured lactic acid, whereas other sweeteners such as glycerol, glucose, fructose, and sucrose inhibited corrosion to varying degrees. Food additives such as sodium benzoate conferred some copper protection. This corrosion potential of copper in the solutions was –65 to –70 mV, whereby, galvanostatic polarization curves exhibited little anodic but appreciable cathodic polarization.

Talati *et. al.* (93) investigated the corrosion of copper in tartaric acid solutions containing various food colourants and / or sweetening agents with respect to the concentration of the acid and colourant and temperature at constant acid concentration. The corrosion increases with the concentration of the colourant, whereas at constant colourant concentration, it increases with acid concentration. Copper in 0.05M tartaric acid develops a corrosion potential of –40 mv (vs. SCE.). The addition of colourants or sucrose did not appear to have any effect on the corrosion potential. Galvanostatic polarization curves showed very little anodic but appreciable cathodic polarization. Sodium benzoate raspberryessence, gun tragacanth, dextrin and potato starch appeared to confer some protection to copper in tartaric acid contain such colourants as carmoisine.

The effect of 1-benzoyl-4-phenyl-3-thiosemicarbazide derivatives as corrosion inhibitors for copper in 3M nitric acid solution (94) by galvanostatic polarization and weight loss methods was studied.

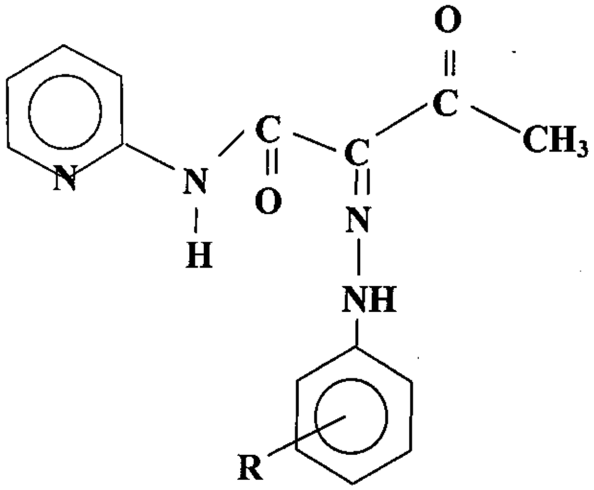


(a) R = p-Methoxy	(b) R = p-methyl
(c) = o-Methyl	(d) = o-Hydroxy
(e) = o-Chloro	(f) = Hydrogen
(g) = p-Nitro	

The used additives act as mixed type inhibitors. The results of polarization measurements carried out for the inhibition efficiency of the additives agreed with those obtained from weight loss. The order of decreasing inhibition efficiency is : a > b > c > d > e > f > g.

The adsorption of these compounds on the surface of copper metal obeys Langmuir adsorption isotherm, but the gradient is not equal to unity as expected for the ideal behaviour. This deviation from unity could be explained on the basis of the interaction between the adsorbed species on the metal surface. The inhibition efficiency of copper in nitric acid solution depends on the polar character of substituents, their molecular structure and concentration.

Fouda *et al.* (95) studied the behaviour of copper in 3M nitric acid containing various concentrations of 2-(Acetoacetamido) pyridinearylhdrazone derivatives as corrosion inhibitors. Galvanostatic polarization and weight loss techniques are used to determine the inhibition efficiency of these compounds over the concentration range $5x10^{-6}$ $-1x10^{-3}$ mol/l. It is evident that nearly complete inhibition is attained at a concentration of 10^{-3} $-4x10^{-2}$ mol/l for all compounds. The order of decreasing inhibition efficiency over the concentration range $5x10^{-6}$ $-1x10^{-3}$ mol/l is : I > II > III > IV > V > VI > VII.



(I) R = 4 – hydroxphenol

(II) R = 3- methoxyphenol

(III) R = 4 – tolyl

(IV) R = Phenyl

(V) R = 3- chlorophenyl

(VI) R = 4- Sulphonyl

(VII) R = 4- nitrophenyl

Effect of potassium iodide on improving copper corrosion inhibition efficiency of benzotriazole in sulfuric acid elelctrolytes was investigated (96). A synergistic effect exists when BTAH and iodide ions are used together to prevent the corrosion of copper in H_2SO_4. The nature of this effect was studied systematically by using electrochemical techniques and XPS. The synergistic effect is due largely to the formation of a film of Cu (IBTA) complex. This new complex film greatly depresses Cu dissolution.

Inhibition of dissolution of copper and zinc in phosphate solution by benzothiazoles (97) was studied. The protective properties of heterocyclic compounds containing two different hetero atoms in their structures were studied. The influence of the polarity of substituents on the inhibiting capability of the organic compounds was determined by using benzothiazole and its two substituted group (R) derivatives (R=H ; NH_2 ; SH ; CH_2CH_2CN ; NH C_2 H_4 ; NHCH3 ; SCH_3 ; SC_2H_5 ; SC(H) ; CH_2 ; SCH_2CH_2CN ; OC_2H_5), as well as benzoxazole and its analogous derivatives, where R = H ; $CH_2SO_2C_4H_9$; and $CH_2SO_2C_6H_5$. The experiments were conducted in a non agitated, naturally aerated 0.5M solution of $NaH_2PO_4.2H_2O$ with PH of 11.7. The inhibitor concentration was varied from $1x10^{-5}$ to $2x10^{-2}$ M. The protective effects were evaluated with the inhibition coefficient calculated from polarization curves $Y = i_o / i_{inh.}$ at E=0.14V (Cu) and E=-1V(Zn), corresponding to the active dissolution range, where i_o and i_{inh}, are the anodic current density values without inhibitor and in its presence, respectively. The corrosion of copper and zinc was determined by weight loss measurements.

Guoding *et. al.*(98) studied the corrosion inhibition of copper by 2-mercapto benzothiazole and benzotriazole in low-conductivity medium (<10 μ s/cm) containing benzotriazole (BTA) and / or 2-mercaptobenzothiazole (MBT) was studied using the a.c. impedance technique, Auger electron spectroscopy and corrosion tests. As the MBT concentration increased, the corrosion rate of copper abruptly rose to a peak, rapidly fell, and then finally decreased steadily. The maximum corrosion rate appeared at a MBT concentration of 0.5ppm. However, a concentration of > 1.5ppm MBT could effectively inhibits copper corrosion. The results from a.c. impedance measurements agreed with those from corrosion tests. The film resistance could be observed only when the MBT concentration was > 1.5 ppm the combination of BTA and MBT was more effective than either compound used alone.

Sankarapapavinasam *et. al.* (99) showed that piperidine, piperidones and tetrahydrothiopyrones were good corrosion inhibitors for copper in sulfuric acid. The effect of piperidine (p), few piperidones [2,6-diphenyl piperidin –4-one; (2,6-DPP); 3-methyl-2,6-diphenyl piperidine-4-one (3-Me-2, 6-DPP); 2,2'-dimethyl-6-one (2,2DMe-6PP); N-Chloro-2,6-diphenyl piperidin-4-one (N-Cl-2,6-DPP)] and the cis and trans forms of 2, 6-diphenylhydrothiopyran 4-one (cis-2 , 6-DP-4-THTP and trans-2, 6-DP-4-THTP) on the corrosion of copper in sulfuric has been investigated by means of spectrophotometric measurements of the metal ions in solution and potentiostatic polarization method. The inhibition efficiency of these compounds has been found to decreases as follows: cis-2, 6-DP-

4-THTP (78%) > trans-2 , 6-DP-4-THTP≅ 3-Me-2 , 6-DPP ≅2, 6DPP(68%) > P(60%) > 2 , 2—DMe-6-PP(55%) > N-Cl-2 , 6-DPP(42%). The inhibitors retard the corrosion process by blocking anodic reaction sites. The negative free energy of adsorption, the positive heat of adsorption and the decrease in apparent free energy of activation in the presence of inhibitors are suggestive of chemisorption of inhibitors on the surface. The inhibition efficiency of these compounds has been explained on the basis of structure depended electron donor properties, mode of adsorption and stability of conformers in the cis and trans forms of 2, 6-DP-4-THTP.

Inhibitory effect 2-mercaptopyrimidine on corrosion of copper single crystal planes in 0.1 M sulfuric acid was investigated *(100)*. Weight loss and polarization techniques were used to investigate the rates of dissolution of copper single crystal (100), (110) and (111) planes in 0.1 M H_2SO_4 as well as in the presence of various concentration (10^{-5}M to 10^{-2}M) of 2-mercaptopyrimidine (2-MP). The corrosion rates of copper single crystal plane were controlled by surface reaction which was found to be a function of crystal geometric orientation, temperature and concentration of 2-MP. The stabilities of the crystal planes in pure acid were found to be (111) > (100) > (110). However, at the critical concentration of 2-MP (10^{-2} M), the order of stability was found to be (110) > (100) > (111). The obtained corrosion data revealed that inhibition on copper corrosion takes place by surface adsorption of inhibitor molecules indicating a Brockris-Swinkels type of adsorption isotherm. Inhibitors efficiencies derived from weigh loss and polarization techniques showed a good agreement. The order of stability of the crystal planes was further confirmed by surface topog. changes during corrosion and also by the thermodynamic parameters of adsorption of inhibitor molecules.

Drogowska (101) explored the passivation of copper in bicarbonate and phosphate aqueous solutions and effect of chloride ions. The present work consists of a comparative study of copper oxidation in bicarbonate and phosphate solutions of pH 8 and their inhibiting effect against chloride ions attack. The phosphate solution had a stronger inhibiting effect against localized attack than did the bicarbonate solution. Voltammograms are given for a copper disk electrode in $Na_2HPO_4$and $NaHCO_3$ solutions with and without NaCl.

The electrochemical behaviour of copper in aqueous solutions of triazinedithiols (TDT) has been studied for the purpose of obtaining the optimum electrolysis condition for surface treatment by Baba *et. al.,*(102) and this by using potentiokinetic polarization , copper electrode showed anodic current peak at a potential around 1.0 V (SCE) in alkaline TDT solutions.

Cicileo *et. al.* (103) were studied the corrosion behaviour of copper in the presence of two organic inhibitors that belong to the oxime group [salycilaldoxime (SO) and benzoinoxime (BO)]. Weight-loss measurements and electrochemical impedance spectroscopy (EIS) were applied to analyse the effect of the organic compounds on the corrosion inhibition of copper in neutral NaCl.

Corrosion behaviour of copper has been investigated by Singh *et. al.,* (104) in different concentrations of formic acid and acetic acid at 30°C by a potentiostatic method . The maximum corrosion rate was found in 20 – 40 mol / l formic acid and in 20 mol / l acetic acid in aqueous solution mixtures. The corrosion rate depended on the concentration of either acid.

Shulan Li. *et. al.* (105) was studied the inhibiting action of some schiff bases on the corrosion of copper in hydrochloric acid. The inhibiting action of these schiff bases has been studied on the corrosion of copper in 5% HCl solution. The potentiostatic polarization and a.c. impedance studies reveal that the inhibiting efficiency increases with a decrease in temperature or an increase in concentration of the schiff bases.

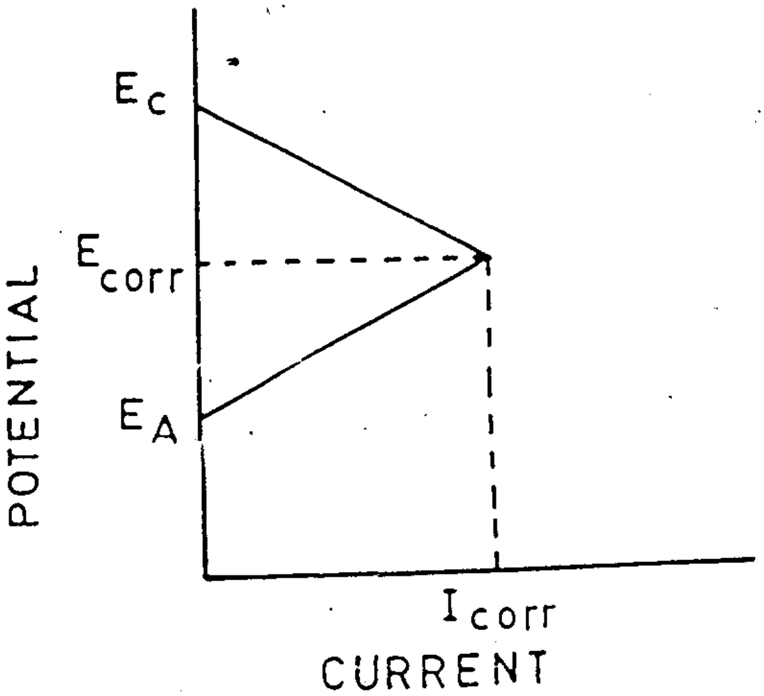


Fig. (1.1): Evans diagram.

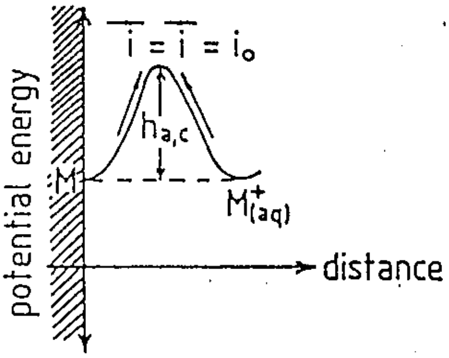


Fig. (1.2): Potential energy vs. distance from electrode surface at equilibrium potential when $\overrightarrow{i} = \overleftarrow{i}$.

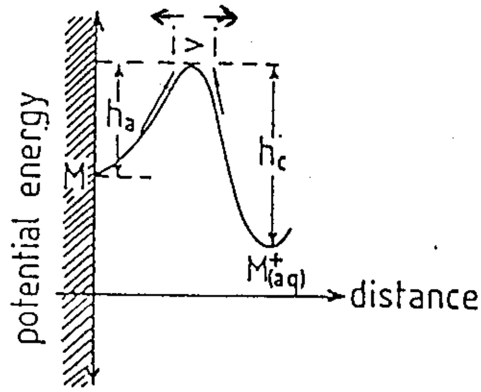


Fig. (1.3): Potential energy vs. distance from electrode surface when potential is made morepositive than E_{eq}.

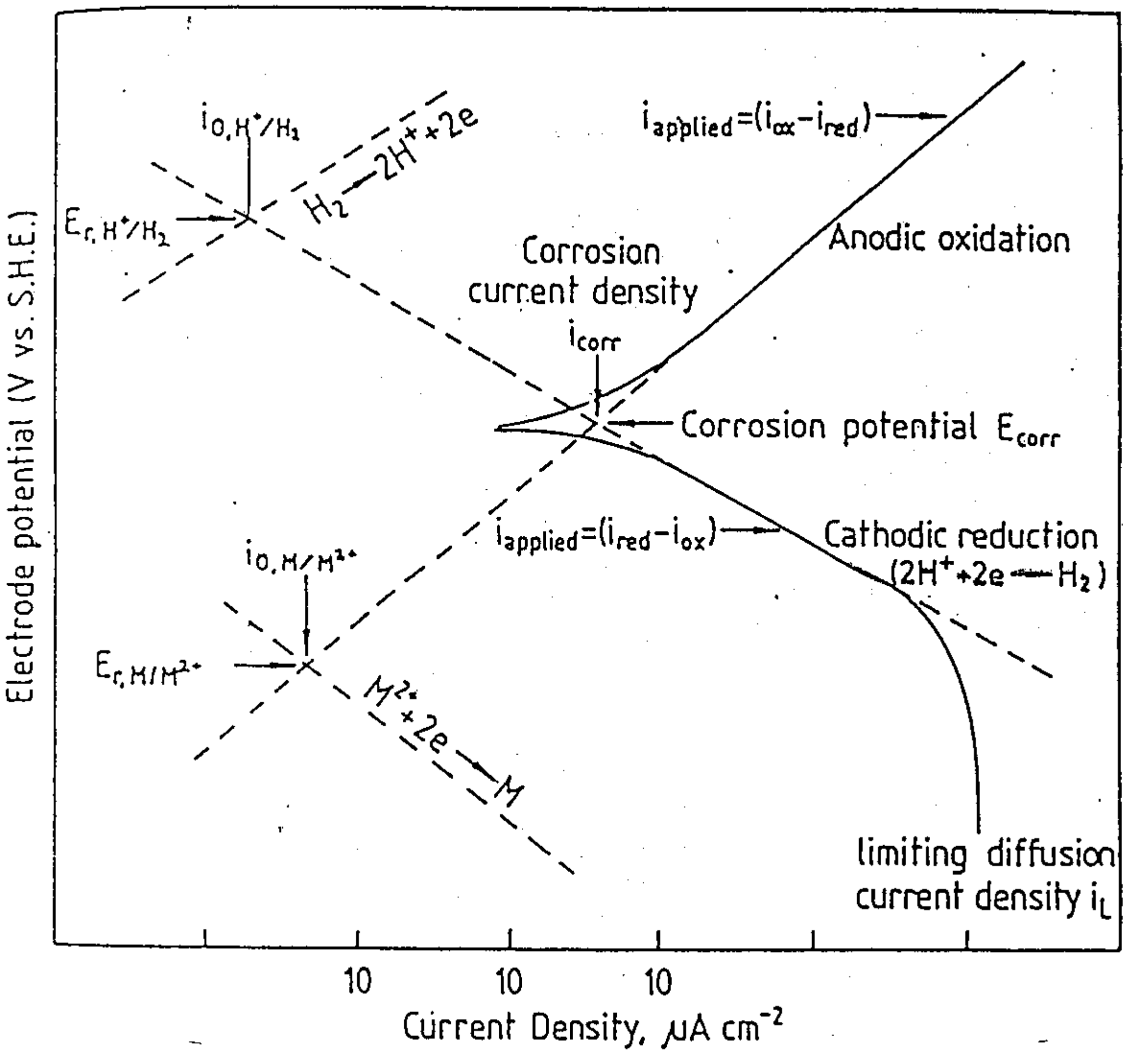


Fig. (1.4): E vs. log I curves for the corrosion of metal in acidic solution in which there are two exchange processes

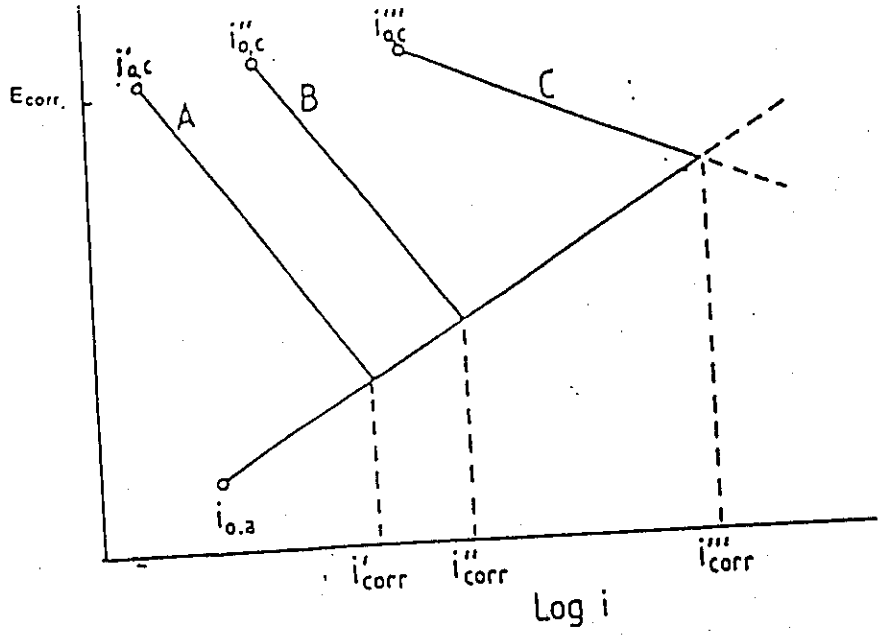


Fig. (1.5): Effect of impurities of different exchange current density for h.e. r.on the corrosion rate of a metal.

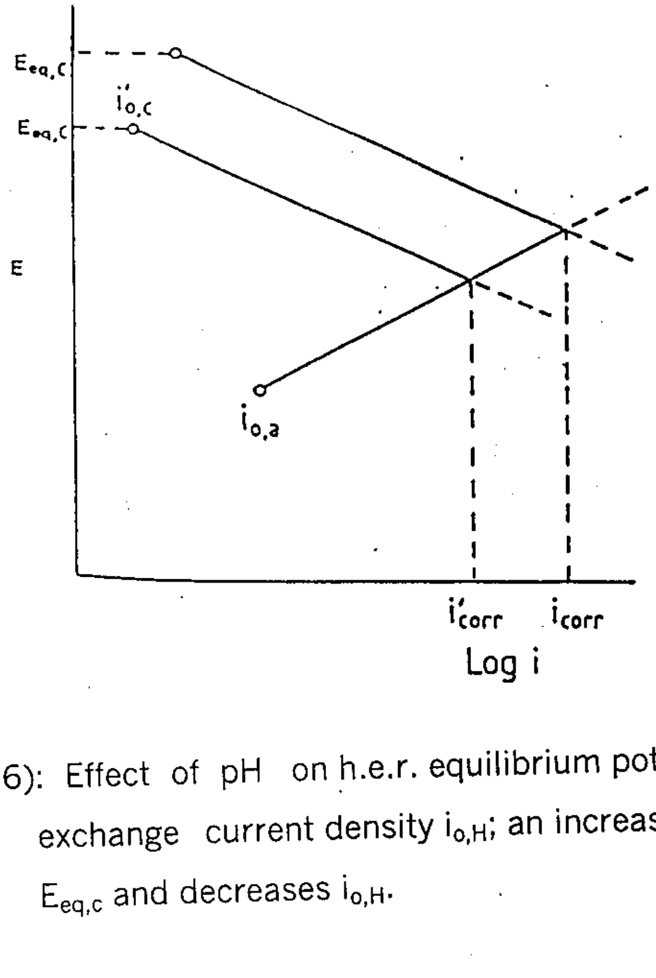


Fig. (1.6): Effect of pH on h.e.r. equilibrium potential E_{eq}. and exchange current density $i_{o,H}$; an increase in pH lowers $E_{eq,c}$ and decreases $i_{o,H}$.

B- Electrical Conductance Measurements

The formation of macromolecule complexes is an ion - molecule reaction, and therefore, the complexation decreases the mobility of the cation (due to the increase in the cation size) rather than in the formation or in the disappearance of the charged species.

Shchori *et al.* (106,107) used electrical conductance measurements to study the complexation of Na^+ with crown ether as example DB18C6, as well as, its 4.4` -dinitro derivatives in DMF and in dimethoxyethane solutions. In a series of solutions containing a constant amount of the metal salt and varying the concentration of the crown ethers, the concentration of free crown ether (L; in any solution) was given by the expression:

$$(L)_{free} = (L)_{total} - (M^+)\,[\,(\Lambda_A - \Lambda) / (\Lambda_A - \Lambda_B)\,] \;\ldots\ldots\ldots\ldots(1.21)$$

where Λ is the equivalent conductance; while Λ_B and Λ_A are the equivalent conductances of the solvated metal salt and the complexed salt, respectively. Due to the relatively low dielectric constant of dimethoxyethane (ε = 7.2) the salt was largely ion-paired, in addition to the usual complexation-constant (K_f) for the reaction.

$$M^+ + L \overset{K_f}{\rightleftharpoons} ML^+ \quad \ldots\ldots\ldots\ldots(1.22)$$

The following equilibra were considered

$$M^+X^- + L \overset{K_{ip}}{\rightleftharpoons} ML^+X^- \quad \ldots\ldots\ldots\ldots(1.23)$$

$$M^+X^- \overset{K_d^A}{\rightleftharpoons} M^+ + X^- \quad \ldots\ldots\ldots\ldots\ldots(1.24)$$

$$ML^+X^- \overset{K_d^B}{\rightleftharpoons} ML^+ + X \ldots\ldots\ldots\ldots\ldots(1.25)$$

The ion-pair dissociation constants (K_{ip}) can be determined according to the method of Fuoss and Accassina *(108)*. Matsura *et al.*, *(109)* and Grünwald *(110)* also used the electrical conductance measurements to study the formation constants of DB18C6 with the alkali ions in DMSO, DMF and PC solutions. In this case, the concentration of the ligand was kept constant and the concentration of the salt was changed. The authors devised the following equivalent conductance of an equimolar solution of an alkali salt (MX) and a crown ether (L):-

$$\Lambda_{obs} = K_s/C = (1-\alpha)\,\Lambda_{MX} + \alpha\,\Lambda_{MLX} \quad \text{..............(1.26)}$$

where (K_s) was the observed specific conductance of the solution, (C) was the concentration of the alkali salt mixed with the crown ether and (α) was the fraction of the cation in the complexed form. Conductance measurements were carried out by Evans *et al.*, *(111)* in methanol and in acetonitrile solutions of alkali salts with DB18C6 and with DC18C6. The measurements were achieved by series of solutions with constant salt concentration but with varying the concentration of the ligand. In general, the addition of crown ether lowered the equivalent conductance of the salt M^+X^- by about 10-15%. The results of these measurements showed that (with DB18C6) the stabilities of complex of Na^+ in methanol is greater than that of K^+, while in acetonitrile the reverse was obtained. Conductometric titration has been used by Pedersen and Frensdorff *(112)* to determine the stoichiometry of the crown ether complexes as example. The results are indicated two types of behaviours. The addition of crown ether to K^+Cl^- solution in methanol showed a decrease in the equivalent conductance due to the decrease in the mobility of the resulted-cation. In stable complexes there will be a clear break at the ligand to metal stoichiometric molar ratio(s), since further addition of the ligand would not affect the equivalent conductance (Λ) of the complexed salt. On the other hand, in non-polar solvents the alkali salt either can be solubilized (as macromolecule complex) or (if in a solution) can be existed predominantly as non-conducting ion pairs. The addition of the crown ether to the suspension of the metal salt in chloroform resulted an increase in the conductance until the stoichiometric molar ratio(s), was followed by a plateau.

1.8 Electrolyte Conductance

In an attempt to understand the complicated problems of electrolyte solutions, the following key Question must be answered: What are the actual kinetic energies in the solution?. It may now be necessary to scope with many kinds of solute entities: ion solvated or unsolvated, electrostatically associated groups of ions, covalency, bound molecules and complex ions. In fact this complex group of electrolyte solutions should be classified into several groups. The familiar division into 'strong' and 'weak' electrolytes prevailed. Instead two main classes: 'associated' and 'non-associated' electrolyte, should be recognized.

1.8.a Non-Associated Electrolytes :

A solute of this kind is believed to exist only in the form of simple cation and anion. This class, although it is small in number, is of great importance in providing some information for straight-forward tests of the theory of the electrolyte solutions. Alkali halides, the alkaline-earth halides and perchlorates, are examples of this kind.

1.8.b Associated Electrolytes :

The associated electrolytes can be subdivided into two classes:

1- **Weak Electrolytes:** The term 'weak electrolytes' is used to described the cases in which the solute can exist as undissociated covalent molecules as well as ions. All acids belong to this class; even the 'strong' halogenated acids and perchloric acid are weak electrolytes in terms of this difinition, since there is no doubt that, at high enough concentrations, the molecular form does exist. Bases are usually weak electrolytes, except for the alkali metal and the quaternary ammonium hydroxides.

2- **Ion-Pairing Electrolytes:** The term 'ion-pairing' is used in discussing a class of electrolytes in which association occurs as the results of purely electrostatic attraction between oppositely charged ions. This concept was introduced by Bjerrum (113) shortly after the appearance of the Debye-Hückel theory,(114,115) and has proved to be an extremely useful concept in interpreting the behaviour of a large class of electrolyte solutions of which the bivalent metal sulfates in aqueous solution form an outstanding example. Almost all salts in non-aqueous solvents show evidence of this effect.

1.8.c Theories of Electrolyte Solutions:

The first satisfactory theory of ionic solution was that proposed by Arrhenius in 1887 which has been mentioned in Antropov's book (116). The theory was based largely on studies of electric conductance by Kohlrausch, colligative properties by Van't Hoff, and chemical properties such as heats of neutralization by Thomsen. Arrhenius was able to bring together the results of these diverse investigations into a broad generalization known as the theory of electrolytic dissociation. Although the theory proved to be quite a useful attempt at describing weak electrolytes, it was soon found to be unsatisfactory for strong and moderately strong electrolytes. Accordingly, many attempts were made to modify or replace Arrhenius ideas with better ones, and finally, in 1923 Debye and Hückel (114,115) put forth a new theory. It was based on the principles that strong electrolytes are completely dissociated into ions in solutions of moderate concentration and that any deviation from complete dissociation is due to the interionic attractions. Debye and Huckel expressed the deviations in terms of activities, activity coefficients, and ionic strengths of electrolytic solutions.

1.8.d Debye-Hückel Theory (114,115)

In 1923, Debye and Hückel presented a simple theory of interionic-attraction effects, which, nevertheless, retains all the essential features in the limit of infinite dilution. Their results have been of enormous value in the practical treatment of electrolyte solutions by providing a limiting law for the extrapolation to zero concentration not only of activities but also of heat, concentrations, heat capacities, volumes, etc. Debye and Hückel (114,115) accepted Ghosh's basic idea that the distribution of ions peculiar to the crystals, where each ions is surrounded predominantly by ions of opposite signs, is retained in solution. There is a continuous interchange between the ions contained in the sphere and the other ions such a statistical sphere around the central ion is called the ionic atmosphere or ionic cloud. All the ions in solution are equal in all respects; each of them is surrounded by an ionic atmosphere and at the same time each central ion makes part of the ionic atmosphere of some other ion (Figure 1.7). It is the existence of ionic atmospheres that distinguishes real electrolytic solutions from ideal ones.

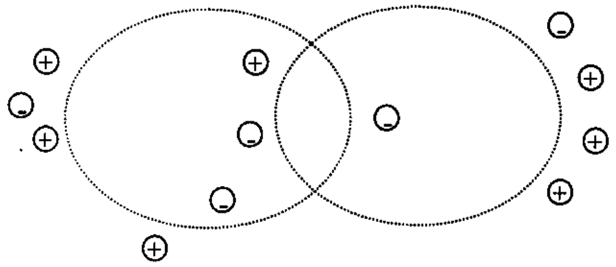


Figure (1.7) The Debye-Hückel model of the ionic atmosphere.

The primary interest in the Debye-Hückel theory is to obtain a limiting law valid in the region of very low concentration for the activity coefficient and other properties. The mean activity coefficient, which is a thermodynamically defined and measured quantity, is given as follows for an electrolyte dissociating into $\gamma +$ ions of charge Z^+ and $\gamma -$ ions of charge Z^-:

$$(\gamma^+ + \gamma -) \ln \alpha^+ + \gamma^- \ln \alpha^- \qquad (1.27)$$

where $\gamma- Z- = - \gamma_+ Z_+$ and finally

$$\ln \alpha_\pm = (8 \pi N_A e_o^2 / 1000 \, DRT)^{1/2} (N_A e_o^2 / 2 \, DRT) (Z_+ Z-) I^{1/2} \qquad (1.28)$$

where N_A is the Avogardo's number, e_o is the electronic charge, D the dielectric constant, T the absolute temperature and I the ionic strength which is given by:

$$I = ½ \sum mi \, Zi^2 \qquad (1.29)$$

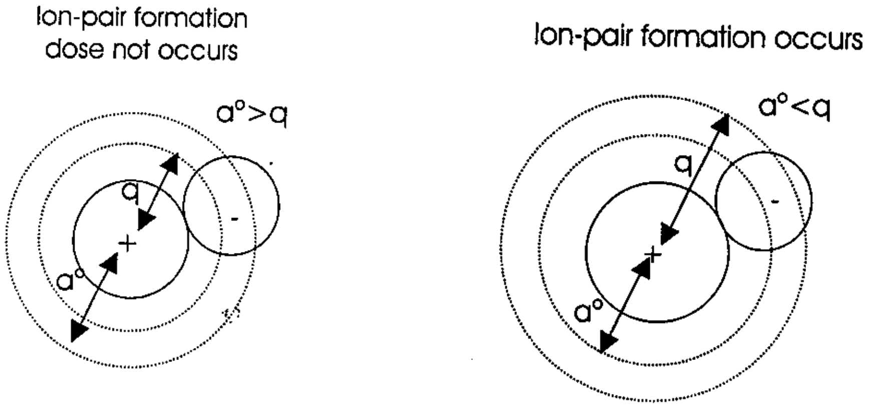
1.8.e. Ion Association (115,117)

The tendency of ions to associate in pairs in large aggregates depends on a balance of coulombic, thermal and solvation forces. Where attractive electrostatic forces between ions are large (when the charge density of ions is high, or when the dielectric constant of the solvent is low), ion-pairs will tend to be formed and will be reasonably stable, existing or periods of time which are lengthy compared with the time required for a single Brownain displacement. For symmetrical electrolytes these ion pairs will have net charge, though they should have a large dipole moment. They will, therefor, make no contribution to the electrical conductivity, while their thermodynamic effects will be of removing a certain number of ions from the solution and replacing them by half the number of dipolar "molecules".

The term ion association was firstly introduce by Bjerrum (113). He used the same model as Debye and Hückel (114,115) and concluded that ion-pair formation occurs when an ion of one type of charge, e.g. a negative ion, enters a sphere of radius (q) drawn around a reference ion of the opposite charge, (a positive ion). It is the ion size parameters which defines the closest approach distance (a°) of a pair of ions. The Bjerrum (113) hypothesis can therefor be stated as follows:

If $a° > q$ the ions remain free;

If $a° < q$ the ion-pairing formation can occur. (Figure1.8)



(a) (b)

Figure 1.8: (a) Ion-pair formation occurs; (b) Ion pair formation does not occur.

According to Bjerrum (113), the final expression for the ion association constant (K_A) is as follows:

$$(\mathbf{K_A}) = \mathbf{4\pi\ NA / 1000\ [Z_iZ_j\ (e_o^2) / DKT]\ {}^{3b}_{2}\!\int e^y\ y^{-4}\ dy} \qquad \mathbf{(1.30)}$$

in which $y = 2q/r$ and $b = 2q/a° = 560\ a°\ D$
for 1 : 1 electrolyte .

Hydrazones have a wide application in synthetic chemistry for the preparation of compounds of most diverse structure and in analytical chemistry for the detection of a large number of metal cations. They are used as plasiticizers, stabilizers for polymers, antioxidants, polymerization initiators, ... etc. They can act as antisoptic agents for wounds, in cosmetics as additives to pharmaceutical products.

Many techniques are found to be useful for the determination of the thermodynamic parameters of the complexation reaction, and can be used for the equilibrium constant determination.

1.9.a Conductmetric Techniques:

The conductance of $Na^{+}I^{-}$ and $Rb^{+}I^{-}$ in AN solutions at 298.15K was measured in the presence of different crown ethers. Analysis of the results in pure AN and in the presence of the crown compounds was carried out according to the Fuoss-Onsager- Skinner equations *(118)*. Addition of the organic ligand to the salt solutions decreased the conductance in the order 12C4 < 15C5 < 18C6 < disubstituted 18C6. The results are also compared with those of $K^{+}I^{-}$ systems and were discussed in terms of competitive interaction forces of the crown ethers and the solvent molecules on the ionic species presented in the solution.

Complexes can also be formed between DB18C6 as organic ligands and alkali earth cations in DMSO, DMF and AN and their stability constants were determined conductometrically *(119)*, at 298.15 K and 308.15K. The stability constants were increased in the order of $Ca^{2+} > Sr^{2+} > Ba^{2+}$ in all solvents. These results were explained in terms of ion cavity radius concepts, solvent basicity and to the solvation of the cations.

Ion association constants were determined for $K^{+}(SCN)^{-}$ in chlorobenzene mixtures with aprotic solvents (AN;DMSO and PC) at 298.15-348.15° K in presence of DB18C6, 18C6 or cryptand 222 by conductometric titration*(120)*. The effect of the solvation and the complexation on ion-pairing were discussed. The stabilities and the selectivity of the complexation of 18C6 and DB18C6 with alkali metal ions, in various solvents were studied in detail.

Smid *et al.* (121,122) showed that the interactions of crown ether polymers with alkali salts in solution can be followed conductometrically. However, the break at the stoichiometric molar ratio was not as sharp as with the monomer since there may be a problem of obtaining a fully cation-saturated polymer solutions.

Nae and Jagur (123) used conductometric measurements to follow the interations of number of crown ethers with organic acids in 1,2-dichloroethane solutions. The formation constant of the complexes constants and the ion-pair dissociation constants were determined according to equations (1.31) and (1.32), respectively:-

$$H^+X^- + L \overset{K_f}{\rightleftharpoons} LH^+X^- \;\;\ldots\ldots\ldots\ldots\ldots\ldots (1.31)$$

$$LH^+X^- \overset{K_d}{\rightleftharpoons} LH^+ + X^- \;\ldots\ldots\ldots\ldots\ldots\ldots (1.32)$$

The association constants (124) of the formation of complexes between the bis(4-tetra-butylbenzo) –18-crown-6 or bis (3,5-di-tetra-butylbenzo)-18-crown-6 with alkali metal cations in MeOH, DMSO and in AN were determined conductometrically and potentiometrically at 298.15 K. The results obtained were compared with those obtained from the polyether DB18C6. It was shown that besides the relative size of the internal hole of the macrocyclic polyether and the metal ionic diameter, the complex formation was affected also by the steric factor and by the physicochemical properties of the solvent used.

1.9.b Polarographic Measurements

Agostiano *et al.* (125) determined polarographically the formation constants of Na^+, K^+ and Cs^+ complexes with DC18C6 in lower alcohols. The values of (K_t, K_f and S) were obtained in the usual manner from the shifts of the cationic half-wave potential upon the addition of the ligand(126,127).

Hofmanova *et al.* (128) studied the complex formation of Na^+, K^+, Rb^+, Cs^+ and Tl (I) with crown ethers; and the stabilities of the complexes were studied in MeOH and in AN by polarographic method. The effect of both, the number of members in the ring and the substituents on the polyether ring, on the stabilities of the complexes were discussed. The character of the solvent was an important factor because of its ability to solvate the cation. In MeOH, where the alkali cations were solvated almost as much as in H_2O, the stability constants of Na^+ complexes were lower than those in AN. With the exception of the 30-membered ring ligand, which is encircling the metal ion on all sides, the polyethers have a planar conformation in their complexes and the cation was not screened off from its surroundings and may co-ordinate 1 or 2 solvent molecules or anions.

The reactions of In (III) with 18C6, DC18C6, 15C5 and B15C5 were investigated in aqueous solutions using d.c. and a.c. polarographic measurements (129). The log β_1 values for the complexes formed at 298.15± 0.1 K were also determined.

The complex formation of Hg^{2+} with some macrocclic crown ethers in nitrobenzene, AN and DMF solutions were studied by differential pulse polarographic (130) at 298.15 K. The stoichiometry and the stability of the complexes were determined by monitoring the shift in the Hg^{2+} differential pulse peak potential against the ligand concentration. The stability of the resulting 11 complex vary in the order DC18C6 > 18C6 > 15C5 > DB18C6 > DB24C8 > B15C5> 12C4. There was an inverse relationship between the complex stability and the Gutmann's donor number of the solvents.

The thermodynamic stability constants (131) of the 1:1 complexes of Na^+ ions with 18-crown-6 (16C6) in aqueous-2-propanol (20,40,60,80 weight % of 2-propanol) at 283.15-318.15 K were determined by the method of e.m.f. voltaic cells without transfer . The values of free energies, enthalpies, and entropies of the complexations were calculated.

1.9.c Potentiometric Measurements

The calculation of the formation constant of any complex can be done in any solvent if one can determine the concentration of the free metal ion (or the ligand) in a solution containing known stoichiometric amounts of the ligand and the metal salt. Potentiometric determinations of the free metal ions by using ion-selective electrodes are simple and can be carried out at very low concentrations of the free metal ion thereby allowing the determination of the stability constants of very stable complexes. It should be noted that indicator electrodes used for such measurements are "cation selecive" and not "cation specific". Consequently, small amounts of impurities may have serious effects if the studies are carried out in very dilute solutions.

An important limitation of the potentiometric techniques is that they are rarely suited to non-aqueous solvents since the behaviour of the electrodes commonly becomes irreversible and erratic. Even in water-like solvents (such as the lower alcohol) selective ion electrodes must be carefully preconditioned before using (132). The problem is strongly in aprotic solvents where very few careful measurements with cation-selective electrodes are known.

A very careful potentiometric studies of large number of crown complexes with the alkali cations, as well as, with ammonium and silver ions were reported by Frensdorff (132). Measurements were made in water and in methanol solutions. A silver-silver chloride electrode was usually used as the reference one, except for the studies of the silver complexes, where it was replaced by the calomel electrode.

1.9.d Calorimetric Techniques

Calorimetric techniques are extremely useful for the determination of the thermodynamic parameters of the complexation reactions. Also, it can be used for the aquilibrium constant determination. If (ΔH°) of a reaction is known and (q) is the measured heat of this reaction for a given solution per kilogram of the solvent, the concentration of the complex in molal units is ($q/\Delta H^{\circ}$) and, therefore;

$$K_{conc.} = \frac{q/\Delta H^{\circ}}{(C^{tot}_{M} - q/\Delta H^{\circ})(C^{tot}_{L} - q/\Delta H^{\circ})} \qquad \text{...........(1.33)}$$

where C^{tot}_{M} and C^{tot}_{L} are the total concentration of the metal ion and of the ligand , respectively .

Izatt and his co-workers *(133-135)* carried out calorimetric studies of numerous crown ether complexes. The formations of 1:1 and 2:1 complexes of the crown ether 12C4 with mono-and bivalent cations were studied in methanol solutions by calorimetric, potentiometric and by conductometric titration *(136)*.

The complexation reactions between different amines and the macrocyclic ligand 18C6 were studied by Buschmann *(137)* in methanol. Calorimetric titration was used to determine the stability constants; the reaction enthalpies and the entropies of these reactions. The stability constants of all amines studied were within the same order of magnitude. However, alkyl and aryl substituents strongly influenced the values of the reaction enthalpies and entropies. In contrast, for all secondary and tertiary amines examined nearly identical values for the reaction enthalpies and entropies were observed. As a result to that the number of hydrogen bonds formed between the crown ether and these amines were not the most important factor. On the other hand, Markova and his workers *(138)* used the calorimetric tichnique to derive the thermodynamic properties of the complexation of NH_4Cl with 18C6 in aqueous solutions at 298.15 and 315.15 K.

Finally, the thermodynamic parameters (log.K, ΔH and TΔS) of the interaction of metal ions with dibenzo-16-crown-5 and its derivatives *(139)* were determined by the solution calorimetry in methanol at 298.15K. The above-mentioned ligand and its derivatives were studied as a metal carrier in bulk liquid membrane (BLM) and as a supported liquid membrane (SLM).

1.9.e Spectroscopic Techniques

Many spectroscopic techniques such as proton magnetic resonance (PMR), ^{13}C-NMR, ^{23}Na=NMR, ^{133}Cs-NMR, ^{205}Tl-NMR, ^{7}Li-NMR, ^{39}K-NMR and ^{87}Rb-NMR, were used for studying the complexation between many cations and many macrocyclic ligands *(140-142)*.

Ultraviolet-visible spectroscopy was used for the study of macrocyclic complexes. Pedersen *(112)* reported changes in the UV-spectra of benzene-substituted crown ether upon complexation. For example, upon the absorption of KSCN-DB18C6 in methanol is showed a new absorption band about 6nm to the larger wavelength side of the major peak. Similar results were obtained by Tusek *et al.*(124) Shchori *et al.*(143) determined the stability constants of several DB18C6 complexes in aqueous solutions by combining the solubility data of the crown ether with the data of the spectrophotometric determination of the total complex concentration.